ELSEVIER

Thermochimica Acta 355 (2000) 171–180

thermochimica acta

www.elsevier.com/locate/tca

Computational aspects of kinetic analysis. Part E: The ICTAC Kinetics Project—numerical techniques and kinetics of solid state processes

B. Roduit*

AKTS Corp., P.O. BOX 240563, Charlotte, NC 28224, USA

Received 8 July 1999; accepted 19 August 1999

Abstract

This is Part E of a series of papers that present the kinetic results computed for a hypothetical simulated process and experimental data for the thermal decompositions of calcium carbonate and ammonium perchlorate. The results show that model-fitting techniques are successful in correctly describing the decomposition of solids when assuming multi-step kinetic models. The multi-heating rate data should be used for the kinetic calculations because the application of the single-heating rate data may fail to disclose the complexity of the process. The comparison of the kinetic parameters obtained from isothermal and non-isothermal experiments is presented and discussed. The results indicate that the proper consideration of the experimental conditions at which the reaction has been investigated should be taken into account for a correct interpretation of kinetic data of solid–gas reactions. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Kinetics; Decomposition; Solids; Model-fitting techniques

1. Introduction

A reliable numerical technique applied to solid state kinetics should be able to provide the following:

1. The best (a) kinetic models (type of model and reaction order), (b) Arrhenius parameters (pre-exponential factor and activation energy), (c) kinetic scheme (one-step, multi-step, parallel, consecutive reactions);
2. The ‘goodness of fit’. Although the goodness of fit does not warrant the correctness of the kinetic description, it is reasonable to expect that a correct model combination can give a good data fit;
3. The possibility of retrieving the kinetics of simulated reaction progresses for which the (a) kinetic models, (b) Arrhenius parameters and (c) kinetic scheme used, have been hidden;
4. A kinetic coherence between the (a) kinetic models, (b) Arrhenius parameters and (c) kinetic scheme for the same reaction performed under both isothermal and non-isothermal conditions (simulated data). The requirement to retrieve the same kinetic characteristics comes from the concepts which prescribe $d\alpha/dt=Z$ (kinetics characteristics) (non-isothermal mode) to give, after mathematical transformation, the same kinetic characteristics for the isothermal conditions (simulated data);

---

* URL: http://www.akts.com
E-mail address: b.roduit@akts.com (B. Roduit)

PII: S0040-6031(00)00447-0

5. A reasonable agreement between the (a) kinetic models, (b) Arrhenius parameters and (c) kinetic scheme for the same reaction performed under both isothermal and non-isothermal conditions (experimental data). However, comparison of isothermal and non-isothermal data can be marred by some uncontrolled experimental factors.

Furthermore, the computations should be carried out with experimental data obtained from at least two or three different heating rates (non-isothermal) or temperatures (isothermal). Model-fitting methods that use single heating-rate methods should be avoided because they tend to produce highly ambiguous kinetic descriptions. However, multi-thermal history model-fitting techniques can be effectively used to describe the solid state reactions and predict the effect of the experimental parameters. The data should be collected under similar experimental conditions because the kinetic parameters of solid-state reactions are not intrinsic properties of an investigated compound, but can change depending on the experimental conditions applied (PSTA-principle: parametric sensitivity of thermal analysis) [1].

2. One-step and multi-step kinetic schemes, parallel and consecutive reactions

Because solid state reactions usually have a multi-step nature, model-fitting analysis deals with the combination of two or more kinetic models (*n*-order reactions (Fn), Avrami–Erofeev (An), Ginstling–Brounshtein (D4), ...). Depending on the considered reaction performed under different heating rates or at different temperatures, the choice of the correct kinetic models strongly influences the ability to properly describe the progress of the reaction. If the choice of the kinetic models is not appropriate, the latter will not match the data at all. Once the determination of the best kinetic models and optimization of the Arrhenius parameters is achieved, the degree of correlation indicates whether the resulting parameters are 'correlated' or 'dependent' on each other. The degree of correlation determines the possible variation in A_1, E_{a1}, n_1, A_2, E_{a2}, n_2, ... in order to still get an acceptable 'goodness of fit' from a statistical point of view. The ideal is to introduce as few adjustable parameters as possible due to the possible risk of 'overfitting' the experimental data. This error can be easily avoided by the introduction of a statistical criterion which relates both 'goodness of fit' and the eventual necessity of introducing additional models or parameters. Due to the multi-step nature of solid state reactions, the introduction of a supplementary model usually proves to be more advantageous than use of a single model analysis because it considerably improves the quality of fit. Nevertheless, extreme care needs to be taken in introducing additional models, because the goodness of fit does not necessarily warrant the correctness of the kinetic description.

3. Verification of a numerical computation

A simple way to verify if a method of model-fitting analysis is reliable, resides in its ability to retrieve:

- The kinetic characteristics of simulated reaction progress for which the (a) kinetic models, (b) Arrhenius parameters and (c) kinetic scheme used have been hidden (simulated data).
- A coherence between the (a) kinetic models, (b) Arrhenius parameters and (c) kinetic scheme, which have been calculated for the same reaction performed under both isothermal and non-isothermal conditions (simulated data).

If a numerical method is trustworthy and applied with due care, it should fulfill the above expectations. The correct values of the kinetic parameters are known for the simulated data only. In the case of experimental data, agreement between the kinetic models, the Arrhenius parameters, and the kinetic scheme, which have been calculated for the same reaction performed under both isothermal and non-isothermal conditions is another factor that may support the conclusion about the reliability of kinetic computations. Nevertheless, several aspects have to be considered when attempting to describe the kinetics for experimental data. One should keep in mind that disagreement between isothermal and non-isothermal kinetic results may be caused by physical reasons, such as thermal and mass transfer, difference in temperature regions of experiments and/or temperature-ramp required to start each isothermal experiment. When applied to isothermal and non-isothermal experimental data, multi-thermal

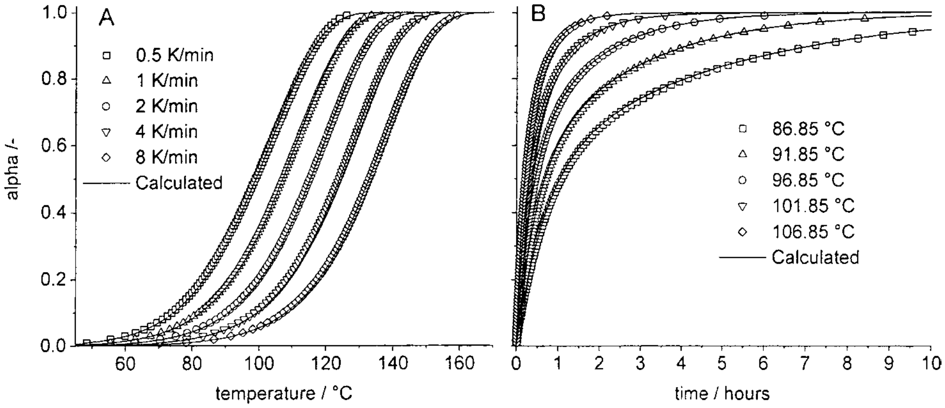

Fig. 1. Reaction extent α as a function of the temperature (non-isothermal, A) and time (isothermal, B) for the simulated data of the ICTAC Project. Simulated data are represented as symbols, solid lines represent the relationships α–T and α–t calculated with the kinetic parameters obtained by Roduit.

history model-fitting methods represent a possible way toward coherent kinetic results.

4. Simulated data

A detailed analysis of the simulated data allows some important observations to be made with respect to the different numerical methods applied by the participants. Three participants (Burnham, Opfermann and Roduit) have found very close kinetic results for the non-isothermal and isothermal simulated data. The calculated parameters found by Opfermann show, however, some deviations depending on the reaction schemes applied in his calculations (concurrent or consecutive reactions). Similar kinetic results to the ones obtained by Burnham, Opfermann and Roduit have also been retrieved by Nomen and Sempere, but for the non-isothermal data set only. In Fig. 1A and B, the simulated data are presented together with the curves α–T and α–t calculated with the kinetic parameters obtained by Roduit. The kinetic characteristics, i.e. kinetic models, Arrhenius parameters and kinetic schemes for both isothermal and non-isothermal conditions are summarized in Tables 1 and 2, respectively. If correctly calculated, the kinetic

Table 1
Best kinetic models and Arrhenius parameters for the non-isothermal conditions of the simulated data of the ICTAC Project

	Burnham	Opfermann[a]	Opfermann[b]	Roduit
Model 1	Fn	Fn	Fn	Fn
$\ln A_1$ (s^{-1})	18.93	21.72	18.79	18.93
E_{a1} (kJ mol^{-1})	80.08	88.1	79.54	80.06
n_1	1.0002	1	1	1
w_1[c]	0.4998	0.533	0.481	0.499
Model 2	Fn	Fn	Fn	Fn
$\ln A_2$ (s^{-1})	30.44	30.79	30.1	30.42
E_{a2} (kJ mol^{-1})	120.11	120.9	118.96	120.04
n_2	1.0003	1	1	1
w_2[c]	0.5002	0.467	0.519	0.501

[a] Consecutive reactions.

[b] Concurrent reactions.

[c] w_1, w_2: Reaction contribution to the total reaction progress.

Table 2
Best kinetic models and Arrhenius parameters for the isothermal conditions of the simulated data of the ICTAC Project

	Burnham	Opfermann[a]	Opfermann[b]	Roduit
Model 1	Fn	Fn	Fn	Fn
$\ln A_1$ (s^{-1})	18.94	21.88	18.948	18.93
E_{a1} (kJ mol^{-1})	80.13	89.04	80.133	80.083
n_1	1	1	1	1
w_1[c]	0.502	0.597	0.502	0.5006
Model 2	Fn	Fn	Fn	Fn
$\ln A_2$ (s^{-1})	30.49	33.22	30.495	30.42
E_{a2} (kJ mol^{-1})	120.26	128.275	120.275	120.04
n_2	1	1	1	1
w_2[c]	0.498	0.403	0.498	0.4994

[a] Consecutive reactions.
[b] Concurrent reactions.
[c] w_1, w_2: Reaction contribution to the total reaction progress.

parameters obtained from the isothermal and non-isothermal data are expected to be the same. For a kinetic scheme involving two kinetic models, the requirement to retrieve the same kinetic characteristics comes from the concepts which prescribe $d\alpha/dt=Z(A_1, E_{a1}, \text{Model 1}, n_1, A_2, E_{a2}, \text{Model 2}, n_2, w_1, w_2)$ (non-isothermal mode) to give, after mathematical transformation, the same set of kinetic results for the isothermal conditions. This kinetic coherence may be verified by comparing the energy differences, $\Delta E=E_{a2}-E_{a1}$, computed for the non-isothermal and isothermal conditions. Burnham, Opfermann and Roduit have retrieved this coherence since their methods have computed the same energy differences ($\Delta E_{\text{non-iso}}=\Delta E_{\text{iso}}\approx 40$ kJ mol^{-1}) for both isothermal and non-isothermal conditions.

Besides the model-fitting analysis, most of the participants have tried to recover the hidden activation energies by applying isoconversional methods (Friedman [2], Ozawa–Flynn–Wall [3–4]). Isoconversional methods are known to allow the calculation of model-independent estimates of the activation energy, $E(\alpha)$, related to different extents of conversion, α. The variation in $E(\alpha)$ as a function of α under non-isothermal conditions have been summarized in Table 3 for low and high α-values, respectively. Since the two reaction models strongly overlap, the dependence $E(\alpha)$ on α does not reflect the same activation energies (about $E_{a1}=80$ kJ mol^{-1} and $E_{a2}=120$ kJ mol^{-1}) and energy difference ΔE ($\approx$40 kJ mol^{-1}) calculated by Burnham, Opfermann and Roduit with model-fitting methods. For the non-isothermal data, the differences ΔE between the activation energies $E(\alpha)$ from low to high α-values are found to be $\approx$30 kJ mol^{-1} (Table 3). This difference in $\Delta E\approx 10$ kJ mol^{-1} corresponds to 25%. Such discrepancies may be larger with greater differences between the E_a-values and/or when the mechanism

Table 3
Estimated activation energies for the simulated data of the ICTAC Project calculated with different isoconversional methods[a]

	Experimental mode	Analysis-type	E_a (low α) (kJ mol^{-1})	E_a (high α) (kJ mol^{-1})	ΔE (kJ mol^{-1})
Burnham	Non-isothermal	F	87.7	117.3	29.6
	Isothermal	F	88.3	129.4	41.1
Li & Tang	Non-isothermal	FWO	85	115	30
Opfermann	Non-isothermal	F	83.3	116.3	33
Roduit	Non-isothermal	F	89.2	117.3	28.1

[a] F: Friedman; FWO: Flynn, Wall, Ozawa.

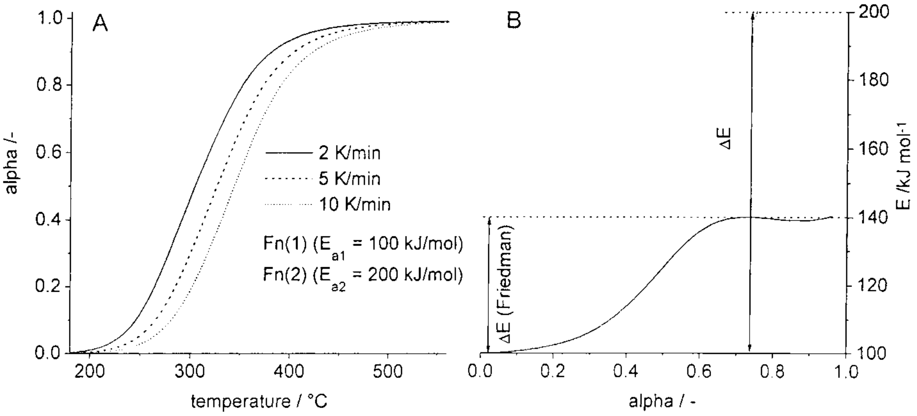

Fig. 2. (A) Simulated reaction extent α as a function of the temperature for a kinetic scheme involving two *n*th-order reactions: Fn(1), n_1=2.167 and Fn(2), n_2=3.432; Arrhenius parameters: $A_1=2.899\times10^6$ s^{-1}, E_{a1}=100 kJ mol^{-1}, $A_2=2.154\times10^{14}$ s^{-1}, E_{a2}=200 kJ mol^{-1}; reaction contributions: w_1=0.753 and w_2=0.247. (B) Dependence of $E(\alpha)$ on α for the simulated reaction progress. Isoconversional method shows a progressive increase of $E(\alpha)$ from 100 to 140 kJ mol^{-1} (Δ*E*(Friedman)=40 kJ mol^{-1} only) for two reactions which activation energies amount to 100 and 200 kJ mol^{-1}.

of the reaction changes during the course of the reaction [5]. The dependence $E(\alpha)$ on α for isothermal conditions shows a progressive increase from ≈88 to 129 kJ mol^{-1} (Burnham, Table 3). These values are higher than the activation energies calculated with model-fitting methods (E_{a1}=80 kJ mol^{-1} and E_{a2}= 120 kJ mol^{-1}). When the kinetic scheme involves two or more different kinetic models, the dependence of $E(\alpha)$ on α can be changed due to the changes in the pre-exponential factors and the exponents '*n*' in the equations of the reaction models. These remarks are illustrated in Fig. 2A and B presenting the simulation of a kinetic scheme involving two reactions characterized by the following kinetic parameters: Fn(1), n_1=2.167 and Fn(2), n_2=3.432; Arrhenius parameters: $A_1=2.899\times10^6$ s^{-1}, E_{a1}=100 kJ mol^{-1}, A_2= 2.154×10^{14} s^{-1}, E_{a2}=200 kJ mol^{-1}; reaction contributions: w_1=0.753 and w_2=0.247. The change in *E* calculated by model-free methods amounts only to 40 kJ mol^{-1} (increase of $E(\alpha)$ from 100 to 140 kJ mol^{-1} from low α to high α-values), whereas the real difference amounts to 100 kJ mol^{-1} (Fig. 2B).

Simulated data are very instructive, since they represent the only test for which the correct kinetic parameters are exactly known. Therefore, they can clearly state if a numerical technique is capable of disclosing the complexity of a process or not. Based on the results obtained by the participants of the Kinetic Project, one can draw the following conclusions:

1. By applying multi-thermal history model-fitting methods properly, it is possible to retrieve the correct kinetic triplets. The latter are identical for both isothermal and non-isothermal conditions.
2. Isoconversional methods estimate variations of the effective activation energy $E(\alpha)$ as a function of α for isothermal and non-isothermal conditions which are alike in form but not identical. The minimum and maximum values of *E* obtained by the isoconversional methods do not necessarily correspond to the values computed with multi-thermal history model-fitting methods.

5. $CaCO_3$ data under nitrogen

For the $CaCO_3$ data under nitrogen, the kinetic results of Burnham obtained with a Sestak–Berggren nucleation model agree fairly well with the values obtained by Opfermann and Roduit who have found very close kinetic characteristics by applying the same kinetic model (*n*th-order reaction (Fn)) to the iso- and non-isothermal data. If we restrict the comparison to the sole activation energies, the values calculated by Burnham, Opfermann and Roduit amount to 194.9,

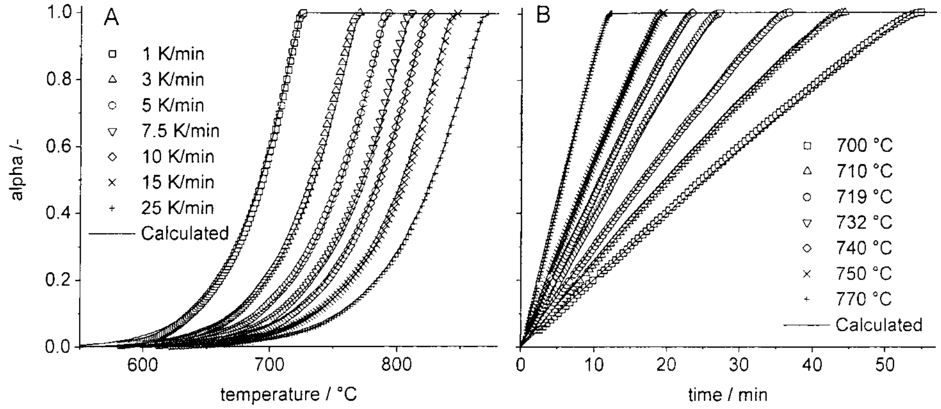

Fig. 3. Reaction extent α as a function of the temperature (non-isothermal, A) and time (isothermal, B) for the $CaCO_3$ decomposition under nitrogen. Experimental data are represented as symbols, solid lines represent the relationships α–T and α–t calculated with the kinetic parameters obtained by Roduit.

192.6, and 194.3 kJ mol^{-1} for the non-isothermal conditions and to 180.3, 178.1, and 181 kJ mol^{-1} for the isothermal conditions, respectively. Decomposition of carbonates is generally described by the phase-boundary reaction (Rn) [6]. This equation has been proposed by Gallagher and Johnson [7] and Salvador et al. [8] for the $CaCO_3$ decomposition under inert atmosphere. The contracting geometry model has been also retrieved by the present author who showed that two models: *n*th-order reaction (Fn) and phase-boundary reaction (Rn) can be used for the description of the experimental data. In Fig. 3A and B, the experimental data for $CaCO_3$ under nitrogen are presented together with the curves of α–T and α–t calculated with the kinetic parameters obtained by Roduit. The kinetic results are summarized in Table 4.

By applying isocoversional methods, the expected kinetic coherence is also retrieved since we obtained nearly identical activation energies for both non-isothermal and isothermal conditions (e.g. Burnham: $E_{\text{non-iso}}=192$ kJ mol^{-1} and $E_{\text{iso}}=190.3$ kJ mol^{-1}). Therefore, both isoconversional and model-fitting methods give rise to activation energies that agree well for both isothermal and non-isothermal data.

6. $CaCO_3$ data under vacuum

Measurements of experimental data carried out under isothermal conditions are usually investigated in a narrow temperature range due to technical problems. Therefore, they may not contain the

Table 4
Best kinetic models and Arrhenius parameters for the non-isothermal and isothermal decomposition of $CaCO_3$ under nitrogen

	Experimental mode	Kinetic model	ln *A* (s^{-1})	E_a (kJ mol^{-1})	*n*
Burnham	Non-isothermal	Sestak–Berggren	15.96	194.9	m=0.011, n=0.176
Opfermann	Non-isothermal	Fn	15.75	192.6	0.146
Roduit	Non-isothermal	Fn	15.86	194.26	0.177
Roduit	Non-isothermal	Rn	15.67	194.26	1.215
Burnham	Isothermal	Sestak–Berggren	14.44	180.3	m=0.087, n=0.155
Opfermann	Isothermal	Fn	14.00	178.09	0.067
Roduit	Isothermal	Fn	14.38	181.01	0.092
Roduit	Isothermal	Rn	14.28	181.01	1.101

Table 5
Best kinetic models and Arrhenius parameters (calculated by Roduit) for the non-isothermal and isothermal decomposition of $CaCO_3$ under vacuum

Experimental mode Temperature range	Non-isothermal $500°C<T<700°C$	Isothermal $515°C<T<550°C$
Model 1	An	An
$\ln A_1$ (s^{-1})	22.85	25.66
E_{a1} (kJ mol^{-1})	204.88	224.24
n_1	1.294	1.527
w_1	0.2909	
Model 2	An	
$\ln A_2$ (s^{-1})	7.51	
E_{a2} (kJ mol^{-1})	102.74	
n_2	2.451	
w_2	0.7091	

information necessary for determining the complexity of a process. The $CaCO_3$ data obtained under vacuum illustrate this problem in a clear manner. For the isothermal conditions, we have an apparent kinetic scheme involving one reaction only (Avrami–Erofeev: An), whereas for the non-isothermal conditions we have to consider two reactions of Avrami–Erofeev type (An(1), An(2), see Table 5). This is due to the fact that the isothermal experiments have been conducted over a narrow range of temperatures (515–550°C) compared to the non-isothermal range of 500–700°C. In such a narrow temperature range, the isothermal reaction progress can be well described using a single kinetic model. Since the ideal is to introduce as few adjustable parameters as possible, the introduction of an additional model is not justified. For the non-isothermal data, however, the necessity of introducing a second model is justified from a statistical point of view, because it considerably improves the quality of fit.

The $CaCO_3$ data collected under vacuum can best be described by a kinetic scheme involving two reactions. As emerges from Fig. 4A, the reaction with the highest activation energy (E=205 kJ mol^{-1}, An(1) in Table 5) appears to be the first reaction for heating rates higher than $\approx$2.5 K min^{-1}. It is followed by the second reaction (activation energy $\approx$103 kJ mol^{-1}, An(2) in Table 5). For a heating rate of $\approx$2 K min^{-1}, the two reaction rates are comparable (Fig. 4A). Therefore, by conducting isothermal experiments over comparable ranges of temperature, we may expect to describe the isothermal reaction progress properly by using only the kinetic triplet characteristic for the first reaction with the activation energy of $\approx$205 kJ mol^{-1}. This expectation is justified, since we retrieve the same kinetic model (An) and similar kinetic characteristics for the isothermal conditions ($E\approx$224 kJ mol^{-1}, Table 5). The first reaction (An(1) with

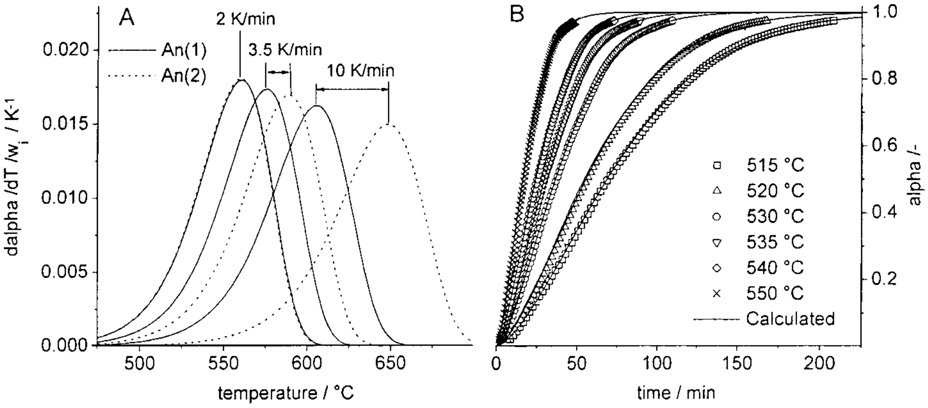

Fig. 4. (A) Derivatives $(d\alpha/dT)/w_i$ as a function of the temperature with the following kinetic parameters: An(1), n_1=1.294 and An(2), n_2=2.451; Arrhenius parameters: $\ln A_1$=22.85 s^{-1}, E_{a1}=204.88 kJ mol^{-1}, $\ln A_2$=7.51 s^{-1}, E_{a2}=102.74 kJ mol^{-1}; reaction contributions: w_1=0.2909 and w_2=0.7091. The use of heating rates higher than ca. 2–3 K min^{-1} helps to discern between the different reactions involved in the kinetic scheme. (B) Reaction extent α as a function of the time (isothermal) for the $CaCO_3$ decomposition under vacuum; experimental data are represented as symbols, solid lines represent the relationships α–t calculated with the kinetic parameters obtained by Roduit.

$E \approx 205$ kJ mol^{-1}) is the rate limiting step of the process for the isothermal conditions and temperature range considered (515–550°C). Therefore, one can estimate the isothermal reaction progress by using only the kinetic triplet characteristic for the first reaction obtained from the non-isothermal conditions. Thus, the aforementioned agreement between non-isothermal and isothermal conditions is also retrieved. This complexity is detectable for non-isothermal data, but does not clearly show up in isothermal data because of the narrow temperature region. Since the sole comparison of the activation energies is very restrictive, the complete kinetic characteristics obtained have been summarized in Table 5. Comparison of the experimental data with the calculated α–t curves is presented in Fig. 4B.

The use of heating rates which are higher than ≈2–3 K min^{-1} helps to discern between the different reactions involved in the kinetic scheme (Fig. 4A). If heating rates are too similar, they narrow the temperature region of non-isothermal experiments, and model-fitting analysis becomes comparable to that using single heating-rate methods and may fail to determine the best kinetic models, just as for isothermal experiments carried over a narrow range of temperatures. Although the activation energies of both kinetic models have been estimated as $E_{a1}=204.88$ kJ mol^{-1} and $E_{a2}=102.74$ kJ mol^{-1}, the dependence of $E(\alpha)$ on α derived from the experimental data is similar to the one derived from the calculated reaction progress (Roduit, Ozawa method: experimental data: $E(0.1)=145$ kJ mol^{-1} and $E(0.9)=115$ kJ mol^{-1}, calculated reaction progress: $E(0.1)=136.2$ kJ mol^{-1} and $E(0.9)=112.4$ kJ mol^{-1}).

7. Ammonium perchlorate data

The kinetic characteristics found by Burnham, Opfermann and Roduit for the ammonium perchlorate decomposition under both non-isothermal and isothermal conditions are summarized in Table 6. Both Opfermann and Roduit were able to describe the reaction progress with a kinetic scheme involving two kinetic models (n-Avrami–Erofeev (An) and nth-order reactions (Fn)) for all heating rates and temperatures of both non-isothermal and isothermal conditions, respectively. They reported very similar reaction contributions of the two reactions amounting ≈23 and 77%, respectively. Burnham described the process with two consecutive Sestak–Berggren models. Nevertheless, a comparison between the activation energy differences $\Delta E=E_{a2}-E_{a1}$ of the two reactions for the non-isothermal and isothermal conditions reveals some discrepancies between the three different numerical methods applied. Agreement between isothermal and non-isothermal kinetic results has been obtained by Roduit, since the activation energy differences ($\Delta E_{\text{non-iso}}$, ΔE_{iso}) computed for the non-isothermal and isothermal conditions are very close (13.2 and 12.5 kJ mol^{-1}). These values found by Burnham amount to 15.3 and 25 kJ mol^{-1}, and those obtained

Table 6
Best kinetic models and Arrhenius parameters for the non-isothermal and isothermal decomposition of ammonium perchlorate[a]

	Burnham		Opfermann		Roduit	
Experimental mode	Non-isothermal	Isothermal	Non-isothermal	Isothermal	Non-isothermal	Isothermal
Model 1	Sestak–Berggren	Sestak–Berggren	An	An	An	An
$\ln A_1$ (s^{-1})	17.11	13.21	14.15	7.96	15.62	15.17
E_{a1} (kJ mol^{-1})	97.7	82.6	92	66.96	99.49	99.28
n_1	$m=1$, $n=1.81$	$m=1$, $n=1.33$	2.26	3.57	2.818	2.922
w_1	0.27	0.27	0.232	0.222	0.2211	0.2357
Model 2	Sestak–Berggren	Sestak–Berggren	Fn	Fn	Fn	Fn
$\ln A_2$ (s^{-1})	15.59	14.28	15.58	14	15.65	15.33
E_{a2} (kJ mol^{-1})	113	107.6	113.43	105.76	112.68	111.76
n_2	$m=0$, $n=0.294$	$m=0$, $n=0.0615$	0.354	0.192	0.467	0.210
w_2	0.73	0.73	0.768	0.778	0.7789	0.7643

[a] The criterion of kinetic coherence prescribes the kinetic parameters obtained from the non-isothermal and isothermal conditions to be the same.

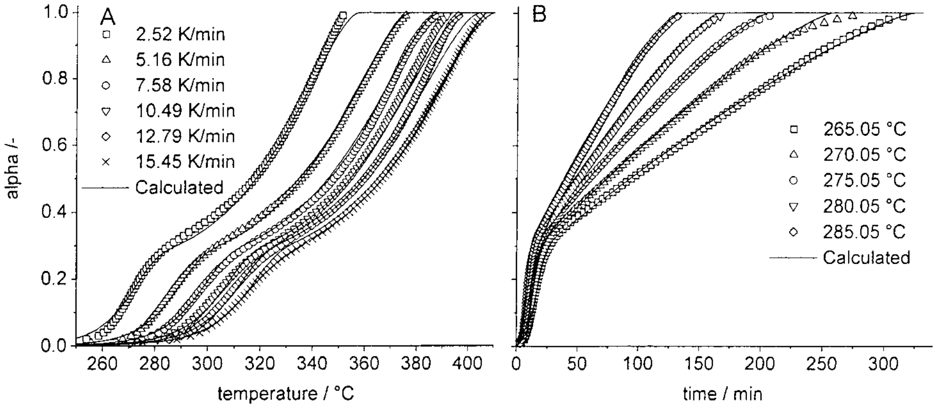

Fig. 5. Reaction extent α as a function of the temperature (non-isothermal, A) and time (isothermal, B) for the ammonium perchlorate decomposition. Experimental data are represented as symbols, solid lines represent the relationships α–T and α–t calculated with the kinetic parameters obtained by Roduit.

by Opfermann to 21.4 and 38.8 kJ mol^{-1}, respectively. Therefore, multi-thermal history model-fitting techniques prove to be stable to the experimental noise and errors which may result from the temperature ramp at the start of each isothermal experiment. By applying an isoconversional method (Friedman), Burnham calculated energy differences of ≈36 and 57 kJ mol^{-1} for low to high α-values. In general, the quantitative coherence of the $E(\alpha)$ dependences of the isoconversional methods can be improved by bringing the temperature regions of isothermal and non-isothermal experiments closer to each other. Nevertheless, this requirement is rarely reached due to experimental limitations (see Fig. 5A and B, $\Delta T_{\text{non-iso}} \approx 160°\text{C}$, $\Delta T_{\text{iso}}=20°\text{C}$). Furthermore, as previously shown for the $CaCO_3$ data collected under vacuum, one should not use similar heating rates in order to bring the temperature regions of isothermal and non-isothermal experiments closer to each other. In Fig. 5A and B, the experimental data are presented together with the curves of α–T and α–t calculated with the kinetic parameters obtained by Roduit.

8. Parametric sensitivity of thermal analysis (PSTA), comparison of the results obtained for $CaCO_3$ under N_2 and vacuum

The kinetic parameters of solid-state reactions cannot be treated as intrinsic properties of an investigated compound because they can change depending on the experimental conditions applied (PSTA-principle [1]). This principle can be illustrated by the experimental data of $CaCO_3$ obtained in nitrogen and vacuum.

The calculations of the kinetic parameters for a given reaction are performed on the basis of data obtained under certain experimental conditions. If for the sake of simplicity, we consider only three experimental variables: the sample mass, S, the flow rate of the gas, F, and the concentration of the reactive gas, C, then a three-dimensional space (S–F–C) containing the possible experimental conditions can be represented as shown in the Fig. 6A. The kinetic parameters calculated from the data obtained under 'arbitrarily chosen conditions' (Fig. 6A, point P: (S_P, F_P, C_P)) are valid for this point and its vicinity in the three-dimensional space. In other words, going from the kinetic description for 'arbitrarily chosen experimental conditions' (point P), one can describe the boundaries within which the experimental conditions can be changed without affecting the estimated values of the kinetic parameters. These boundaries describe a so-called 'isokinetic space' (Fig. 6B) whose size is characteristic of the investigated reaction and for the set of the experimental conditions applied, i.e. it is not the same in different positions in the S–F–C space.

Because the experimental conditions applied for the $CaCO_3$ decomposition under nitrogen atmosphere (S_1, F_1, C_1) and vacuum (S_1, F_1, C_2) are different, one cannot expect model-fitting analysis to lead to the same kinetic characteristics or 'isokinetic space'. As emerges from Table 4, the isothermal decomposition

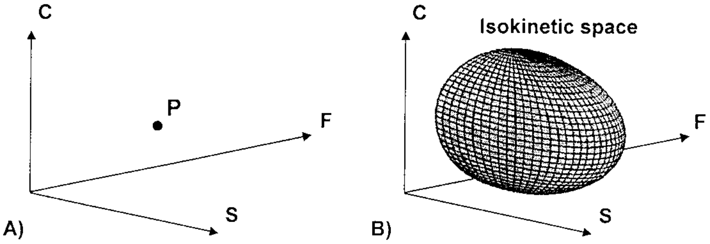

Fig. 6. (A) *S–F–C* space containing the possible experimental conditions: the best model(s) and Arrhenius parameters are calculated from the data obtained under the experimental conditions represented by point P; (B) 'Isokinetic space': the course of the reaction performed under conditions lying outside this space cannot be properly described by the kinetic parameters calculated for the point P.

of $CaCO_3$ under nitrogen atmosphere can be well described with a kinetic scheme involving one reaction (*n*th-order reaction (Fn)) for which the activation energy is $\approx$181 kJ mol^{-1}. However, the same reaction carried out under vacuum follows an Avrami–Erofeev (An) reaction type with an activation energy of $\approx$224 kJ mol^{-1} (Table 5). Similarly, this discrepancy between kinetic models and Arrhenius parameters is observable for non-isothermal conditions (Tables 4 and 5). This example indicates that the failure to give due care to the PSTA-principle can lead to erroneous interpretation of the kinetic results. Statements that "the activation energy of the decomposition of compound 'X' is '*Y*' kJ mol^{-1}" should thus mention the experimental conditions under which the reaction has been investigated.

9. Conclusions

The present study aimed at a global kinetic treatment of the processes occurring during solid state decomposition. Despite the difficult challenges faced, the examples arising from the ICTAC Project clearly indicate that our expectations to find similar Arrhenius parameters and models of the same solid state reaction for isothermal and non-isothermal conditions are correct if the numerical technique is trustworthy and applied with due care. This indicates that multi-thermal history model-fitting techniques may be used efficiently to describe solid state reactions and predict the effect of the experimental parameters. The corroboration of the numerical techniques, when comparing the simulated and experimental data of the ICTAC Project to the calculated reaction progress, is felt to be especially rigorous. Consideration of the wide range of temperatures achieved with non-isothermal experiments provides very important insights in interpreting and quantifying the experimental results and non-isothermal experiments appear to be more advantageous than isothermal conditions. In addition, a proper consideration of the PSTA-principle avoids the incorrect interpretation of kinetic data of solid–gas reactions.

References

[1] B. Roduit, M. Maciejewski, A. Baiker, Thermochim. Acta 282/283 (1996) 101.
[2] H. Friedman, J. Polym. Sci. 6C (1963) 183.
[3] T. Ozawa, Bull. Chem. Soc. Jpn. 38 (1965) 1881.
[4] J.H. Flynn, L.A. Wall, J. Res. Nat. Bur. Standards 70A (1996) 487.
[5] S.V. Golikeri, D. Luss, AIChE J. 18 (1972) 277.
[6] M.E. Brown, D. Dollimore, A.K. Galwey, in: C.H. Bamford, C.F.H. Tipper (Eds.), Chemical Kinetics, Vol. 22, Elsevier, Amsterdam, 1980.
[7] P.K. Gallagher, D.W. Johnson, Thermochim. Acta 6 (1973) 67.
[8] A.R. Salvador, E. Garcia Calvo, C.B. Aparicio, Thermochim. Acta 143 (1989) 339.